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RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F

Sixth Quarterly Status Report

Contract NASr-99

National Beryllia Corporation
Haskell, New Jersey

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National Aeronautics and Space Admin.
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Sixth Quarterly Status Report
for the Period July 1 to September 30, 1963

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ABSTRACT

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The concept of the reduction of the radiation or photon transfer of heat through the pores of a low density ceramic structure at high temperature by the incorporation of various radiation barrier phases into these voids is being investigated. The radial heat flow thermal conductivity metering apparatus has been modified from a graphite helix to a graphite hair-pin heater design, simplying specimen changing and temperature measurement. Thermal conductivity data up to specimen hot face temperatures of 4235°F are reported for zirconia foam samples.

Descriptions and photomicrographs of ceramic foams containing metallic thermal radiation reflecting phases are presented. Preliminary data on graphite radiation scattering phases are included.

A reprint of a technical paper describing the thermal conductivity test cell is appendixed.

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TABLE OF CONTENTS

1. Introduction

1.1 Purpose of the Program

1.2 Phases of the Program

2. Discussion

2.1 Phase I - Technical Review

2.2 Phase II - Materials Formulation

2.2.1 Aromatic Hydrocarbons

2.2.2 Carbon Systems

2.2.3 Metallic Tungsten

2.2.4 Molybdate Systems

2.3 Phase III - Experimental Measurements

2.3.1 Thermal Transfer Cell Modifications

2.3.2 Data Revision

2.3.3 Composite Measurements

3. Conclusions

4. Program for Next Quarter

5. References

6. Appendix I - Thermal Conductivity Measurements Between 1000 and 2500°C.

Appendix II - Sample Calculations

(1) INTRODUCTION

1.1 Purpose of the Program

Low density foamed ceramic thermal insulation rapidly looses efficiency above 2400°F due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low density refractory structure. Mechanisms such as absorption and re-radiation by embedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

1.2 Phases of the Porgram

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during the sixth quarter discussed in Section 2.

Phase I - Technical Review

Review of previous high temperature heat transfer work, essentially completed during the first quarter, has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

Phase II - Materials Formulation

The major effort of the program is concerned with the fabrication of low density, low apparent thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding

phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity has been previously reported have also been prepared for calibration and equipment checkout purposes.

Phase III - Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell capable of maintaining, under steady state conditions, specimen hot-face temperatures of 4500°F has been fabricated and calibrated. Measurement of the apparent (total) thermal conductivity of the ceramic foam composite test samples is in progress.

(2) DISCUSSION

2.1 Phase I - Technical Review

An excellent analysis of radiation heat transfer in insulation materials is presented in a recent report by Wechsler and Glaser[1] they conclude, through a review of previous work and theoretical considerations, that increasing the absorption and scattering cross-sections of an insulation material will decrease the radiation contribution to thermal conductivity. Although many assumptions and simplifications were made in their analysis of radiation and conduction in insulating media, they further predict that decreasing particle size and emmisivity and increasing the reflectivity of particle surfaces should reduce radiant energy transmission at high

temperatures. In experimental portions of their work, concerned primarily with evacuated thermal insulation systems, they compile and present thermal data on currently commercially available insulating materials. Among their concluding recommendations they suggest "Thin sheets or small plates of refractory materials coated with reflective materials and properly oriented should be examined".

A technical paper describing the thermal conductivity test apparatus developed for the present program was prepared for presentation at the Third Annual Thermal Conductivity Conference, sponsored by the Oak Ridge National Laboratory, at Gatlinburg, Tennessee, October 16 - 18, 1963. This paper is reproduced as Appendix I of this report.

2.2 Materials Formulation

2.2.1 Aromatic Hydrocarbons

Efforts to produce large thermal conductivity test specimens of zirconia foam Code Zr28 containing carbonaceous deposits within the foam pores from the thermal decomposition of aromatic hydrocarbons have been unsuccessful. Although preliminary results on small samples were promising, it was evident that in more massive specimens a large percentage of the hydrocarbons volitalized prior to thermal decomposition in the reducing atmosphere. This hydrocarbon evaporation, was troublesome in that carbon deposits caused electrical leakage and premature failure of the resistance heated furnaces. Although

this situation could be overcome by alternate furnace design, additional efforts on this method of radiation barrier phase incorporation will be delayed until other, less troublesome methods are evaluated.

2.2.2 Carbon Systems

Additional measurement specimens of foam Zr28 containing graphite phases added by the two methods measured earlier[2] to 3000°F have been prepared. Conductivity data on a set of specimens prepared by one of these methods, i.e., aqueous impregnation of colloidal graphite into the fired sample, are presented in Section 2.3.3. Samples prepared by the alternate approach of adding graphite particles as a raw material and sintering the ceramic foam in an atmosphere furnace, await measurement at the higher temperature now available.

2.2.3 Metallic Tungsten

Two methods of preparing fired ceramic foam conductivity specimens containing tungsten heat reflecting phases have been successfully developed. Figure 1 is a photomicrograph at 50X of a fired zirconia foam of the Zr28 type but containing five volume percent of hollow zirconia microspheres, each coated with a one to two micron thick layer of tungsten metal. High temperature thermal conductivity measurements of these samples has not been completed. Additional samples containing 10 volume percent are being prepared.

Figure 2 is a photomicrograph at 50X of the same zirconia foam Zr28 but containing five weight percent of fine tungsten

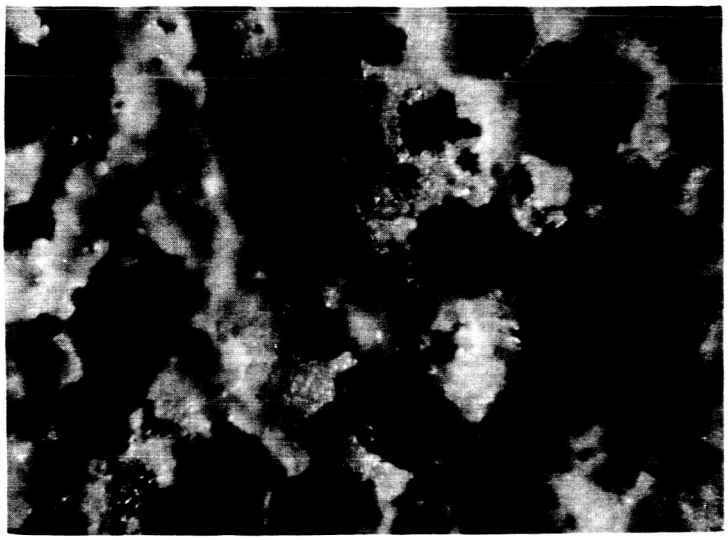
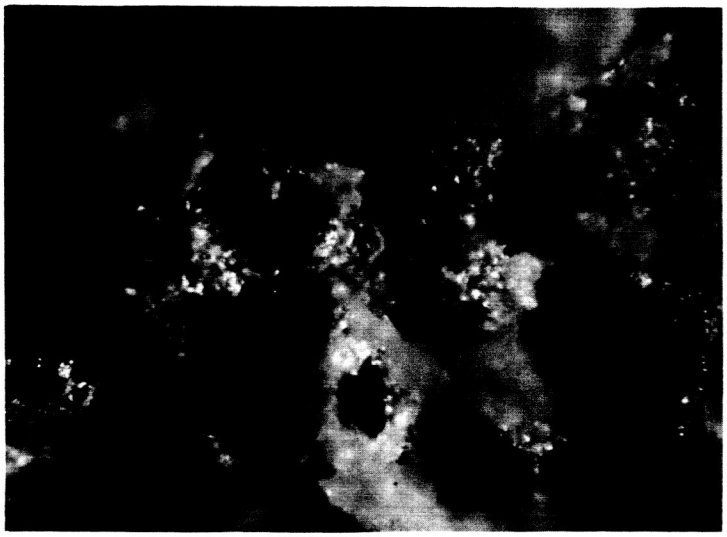


Figure 1

PHOTOMICROGRAPH (50X) OF ZIRCONIA FOAM TYPE Zr28 CONTAINING TUNGSTEN COATED HOLLOW ZIRCONIA SPHERES.



100X

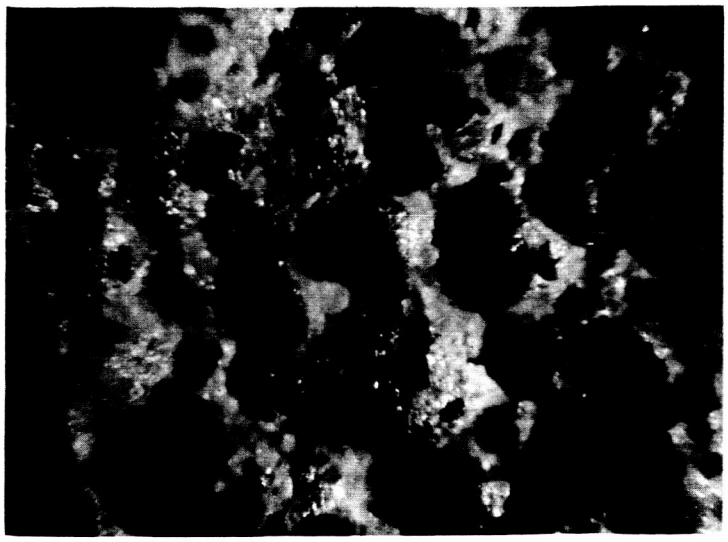


Figure 2

PHOTOMICROGRAPH (50X) OF ZIRCONIA FOAM TYPE Zr28 CONTAINING 5 WEIGHT PERCENT TUNGSTEN PARTICLES.

flakes. Samples containing both five and ten weight percent of this addition have been prepared, fired, and machined and await thermal conductivity measurement.

2.2.4 Molybdate Systems

Attempts to incorporate metallic radiation reflecting phases into a Zr28 matrix by a method similar to solution metallizing of pure oxide ceramics for electronic applications have been unsuccessful. One such specimen, saturated with a lithium molybdate metallizing solution then subsequently dried, was assembled in the thermal conductivity test cell for Run #21. At only moderate hot-face temperatures (3000^{o}F) in an atmosphere of dissociated ammonia; the sample failed catastropically damaging the hair-pin heater and other internal components of the apparatus. X-Ray data of the failed sample indicated the normal phases present, cubic zirconia, molybdenum metal, unreacted lithium molybdate and several unidentified diffraction peaks not corresponding to zirconium carbide or other possible (if improbable) compounds. Additional attempts using alternate solutions such as ammonium molybdate will be attempted, however, the precaution of pre-reaction in a less complex atmosphere furnace will be employed.

2.3 Phase III - Experimental Measurement

2.3.1 Thermal Transfer Cell Modifications

Conversion of the thermal transfer cell to the graphite hair-pin heater design proposed in the Fifth Quarterly Status Report[2] has been completed as described in Appendix I of this report.

Runs #18-22 described in Section 2.3.3 were made using this design. Specimen hot-face temperatures of 4300°F are now readily available. Uniform temperatures appreciably higher than this appear impractical with the hair-pin design in the argon atmosphere because of high current leakage through ionized argon gas between the slot of the graphite heater, causing high local temperatures (above the melting point of zirconia). This temperature range could be extended theoretically to at least 6500°F but the increased complexity and cost is not justified in this evaluation program.

Other minor modifications include the power terminal arrangement on top and the vacuum bell system on the bottom of the device. Power terminals were changed from stainless steel to brass and then back to a modification of the original water-cooled nickel. Space limitations and the necessity for a vacuum tight seal (about 10^{-3} mm of mercury) required several mechanical modifications of the top terminal arrangements before a practical, leak tight and cool running arrangement was developed.

Oxidation of the graphite phase in the sample of Run #20, presumerably due to air entrapped within the zirconia foam, necessitated the use of the bottom vacuum bell so that the chamber could be evacuated to 1 micron pressure, then backfilled with argon prior to measurement. This technique, employed in Run #22 in which tungsten flake samples were to be measured, resulted in back streaming

of oil vapors which obscured sight windows. For this reason vacuum valve systems were added to the lower vacuum bell.

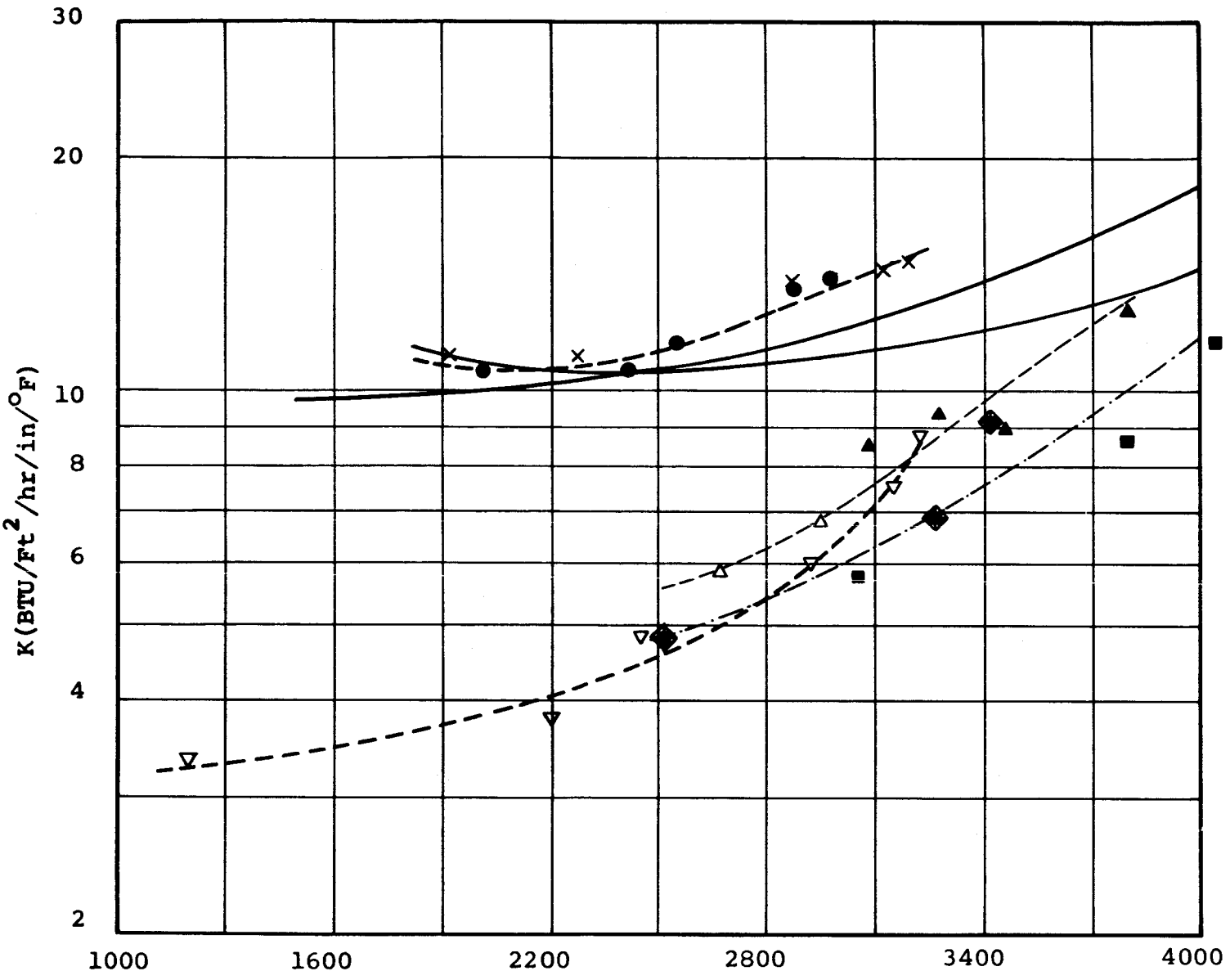
2.3.2 Data Revision

In the preparation of the technical report of Appendix I thermal conductivity data were re-calculated into watts per centimeter degrees C units ($W/cm^{o}C$) required by the thermal conductivity conference publications instructions. In the course of this recalculation a systematic error in previously calculated and reported thermal conductivity data was uncovered. For this reason a corrected sample calculation is presented in Appendix II.

2.3.3 Conductivity Measurements

Figure 3 is a revised thermal conductivity vs. temperature plot of several selected previously reported thermal conductivity measurements. It may be noted that all curves are uniformly displaced downward, towards values of lower total apparent thermal conductivity.

Measurements of zirconia specimens high fired to 85% of theoretical density, both in early runs using the molybdenum wound heater design and in later measurements in which a graphite helix heater was used, now approach more closely the values reported by Pears[3] for similar specimens. The reason for the slightly higher values at higher temperatures has not been established. Several possibilities are: 1) differences in densities, purity or microstructure of the specimens, 2) thermal end losses from the present apparatus. A water cooled, heat metering end plate, thermally insulated by O-ring seals has been



●NBC Zirconia 85% Dense, Runs 4 and 6

× NBC Zirconia 85% Dense, Run 17

—— SRI Dense Zirconia, C.D. Pears Data (ref. 3)

◆ Zirconia Foam Zr28, Run 15 ■ Inner Gage Section

△ Zirconia Foam Zr28, Run 16 ▲ Inner Gage Section

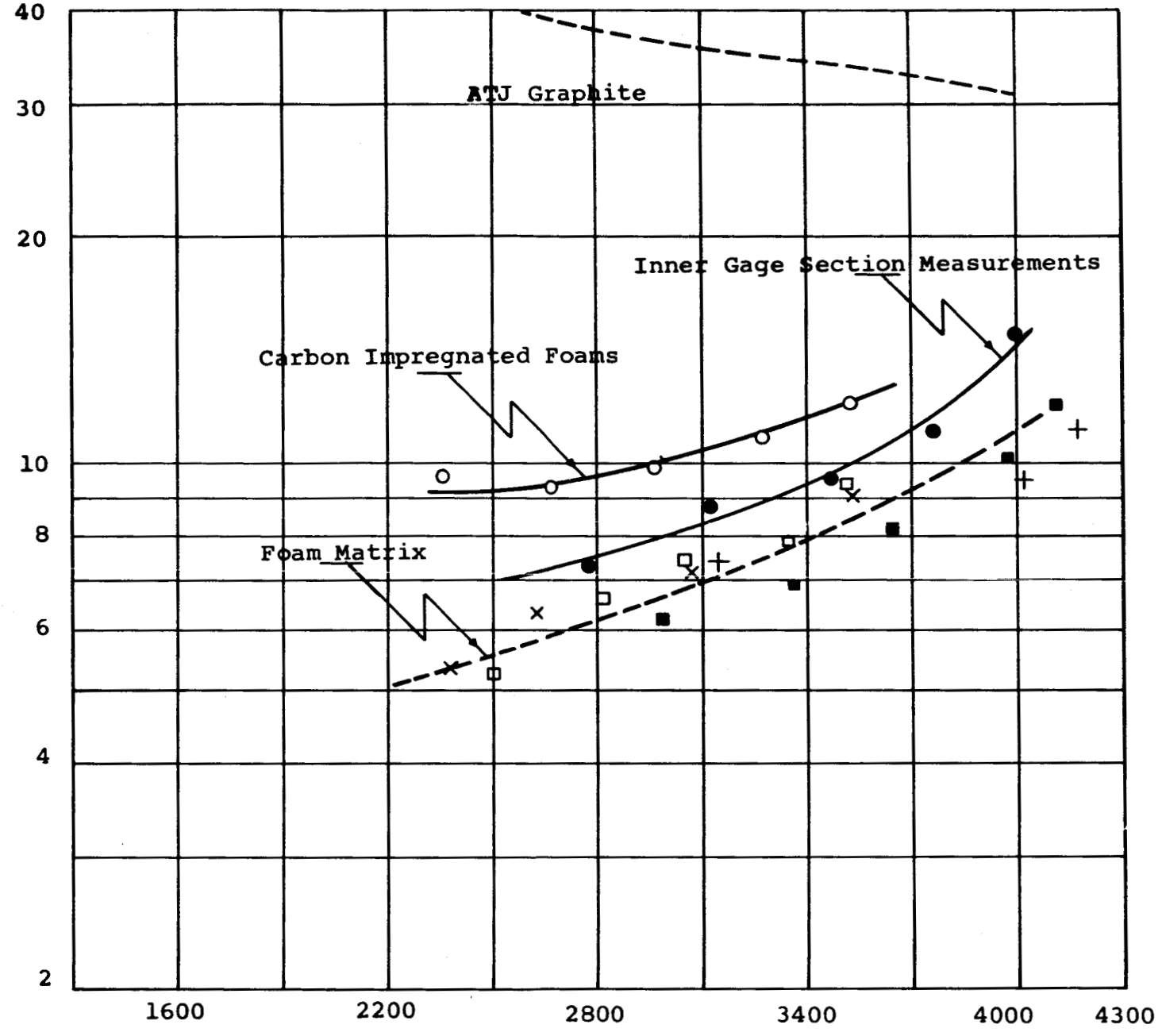
▽ Zirconia Foam Zr6, Run 7

Figure 3
THERMAL CONDUCTIVITY VERSUS TEMPERATURE

prepared so that end losses may be estimated.

Figure 4 contains thermal conductivity data obtained during this quarter. Data for two variations of zirconia foam type Zr28 are shown. Run 18 data are from a specimen of density 0.72 g/cc after firing to 3000°F. Although conductivity increases rapidly above this temperature, little thermal degradation or shrinkage was noted in the specimen surfaces exposed to temperatures in excess of 4100°F. Run 19 data are from identical material but prepared with a higher solids content producing a foam of density 1.3 g/cc after similar firing. This comparison is necessary in that most foams "loaded" with radiation barrier phases have increased densities approaching 1.3 g/cc. Comparative data of matrix and composite would not be valid unless total densities were equal. It may be noted that this small change in density has little effect on total thermal conductivity of the Zr28 type ceramic foam. Again little thermal degradation was observable even in areas adjacent to the heater which was at 4235°F for several hours.

It may be noted that inner gage section measurements, i.e., measurements considering the 1/8" thick section immediately adjacent to the graphite heater, are consistently lower in values than those from the 3/8" thick section well within the specimen. The probable reason for this is that the measured heater temperature is not the same as the specimen "hot face" temperature, but somewhat higher, yielding a high ΔT and therefore a low value of K. Values reported in Figures 3 and 4 of this report are "as measured"



□ Zirconia Foam Zr28, Run 18, Density 0.72 g/cc

× Zirconia Foam Zr28, Run 19, Density 1.3 g/cc

○ Zirconia Foam Zr28, Run 20, Density 0.72 g/cc Impregnated with Graphite to 1.3 g/cc

● Inner Gage Section

----- ATJ Graphite (3)

■ Run 18, Inner Gage Section Measurements

+ Run 19, Inner Gage Section Measurements

Figure 4
THERMAL CONDUCTIVITY VERSUS TEMPERATURE

calculated in accordance with Appendix II. No attempt has been made to "standardize" these values with accepted thermal conductivity standards (because none exist) or to correct the values for the several systematic sources of error mentioned. When sufficient data have been obtained on a variety of specimens estimates may be made of 1) hot face temperatures, 2) end losses, 3) sight hole losses, 4) gas convection losses and 5) other miscellaneous sources of error and suitable corrections applied.

Run 20 data shown in Figure 4 are from a specimen of Zr28 foam, density 0.72 g/cc, vacuum impregnated, after firing and machining, in a colloidal suspension of graphite. This graphite impregnated foam, dried to 1.3 g/cc approximate density, exhibited increased thermal conductivity at initial low (less than 3000^{o}F) temperatures due to the high conductivity of the graphite. Attempts to observe its effect on radiative transmission at higher temperatures were unsuccessful in this experiment because the graphite was, in part, oxidized out during the run. Air either entrapped within the foam or air entering through a faulty terminal seal could be responsible for this oxidation. Accordingly, inner gage section measurements, the area of maximum oxidation, approach the conductivity values of unimpregnated Zr28. This experiment will be repeated when both possible sources of oxidation are corrected.

3.0 CONCLUSIONS

Conductivity runs 18 - 22 have shown the following:

1. The graphite hair-pin heater design is useful to hot face temperatures of over 4200°F.
2. Data from this design modification are directly comparable to data from a graphite helix or molybdenum wound heater.
3. Provision must be made for the removal of entrapped air in ceramic foam insulation containing oxidizable radiation barrier phases.

Large thermal measurement specimens may be fabricated, fired and machined of zirconia foams containing metallic tungsten flake and tungsten coated hollow zirconia spheres as thermal radiation barriers.

4.0 PROGRAM FOR NEXT QUARTER

Reassembly and testing of the conductivity apparatus after the several mishaps and modifications described, will be completed. Specimens of foam type Zr28 but containing tungsten flake, tungsten coated hollow zirconia spheres and several types of graphite fabricated during the last quarter will be measured in the device.

Additional efforts will be directed at the solution metallizing approach of thermal radiation barrier incorporation. Further development of closed pore thermal insulation will continue.

5.0 REFERENCES

1. Wechsler, A. E. and Glaser, P. E., "Investigation of the Thermal Properties of High-Temperature Insulation Materials," ASD-TDR-63-574, July 1963.

2. Styhr, K. H., "Research on Low Density Thermal Insulation Materials for Use Above 3000°F," Fifth Quarterly Status Report, NASr-99, July 1963.

3. Pears, C. D., "The Thermal Properties of Twenty-six Solid Materials to 5000°F or Their Destruction Temperatures", ASD-TDR-62-765, January 1963.

APPENDIX I

THERMAL CONDUCTIVITY MEASUREMENTS BETWEEN 1000 AND 2500°C

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INTRODUCTION

This first progress report will describe an apparatus for the measurement of thermal conductivity which was only in the design stages at the time of last years conference. The device was necessary as an analytical tool in the evaluation phase of a program primarily concerned with the development of thermal insulation materials for use at "hot face" temperatures above 1650°C. Its main purpose is to determine the effect of added thermal radiation barrier phases incorporated within the pores of a low density foamed ceramic structure. Since comparative evaluations of the effect of various added phases on the radiation or photon contribution to total thermal conductivity at high temperatures were required, reproducibility rather than absolute accuracy was important allowing simplification of design requirements.

The measurement technique selected was a direct, steady state, radial heat flow method employing a relatively large sample. Large sample size was desirable because the type of materials to be measured will often contain large pores and high pore volumes. A hollow, right circular cylindrical specimen geometry was therefore chosen. For simplicity, ease of operation and economy an internal heating method was employed.

EXPERIMENTAL APPARATUS

The specimen size chosen was a right circular cylinder 9" high and 2" in outside diameter. This height is normally achieved by stacking two or more shorter cylinders. Radial temperature gradient measurements are made in the central three inch portion of the specimen, the outer regions serving as guard rings. Radial heat flow is established by inserting a long narrow heater into a 3/4" I.D. concentric hole throughout the length of the 9" specimen. Internal heating was chosen because;

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1. The power input is a measure of the heat flow Q passing through the specimen.

2. Complicated and tricky heat sinks may be avoided sacrificying the accuracy of this direct method but not its precision.

3. The specimen itself serves as thermal insulation decreasing the size and cost of the device.

Basically the apparatus consists of a water cooled, steel chamber 10" in internal diameter and 16" high as indicated in the sketches of Figure 1 - 3. Steel end plates, fitted with O-ring seals are attached top and bottom, a second top plate being fabricated to accommodate the heater modifications of Figures 2 and 3. A vacuum bell, not shown, may be fitted at the bottom as desired. Two sight ports, located 180°C apart accommodate 2" diameter x 0.125" thick fused quartz windows also sealed with O-rings.

Primary insulation consists of the specimen themselves, and several concentric molybdenum radiation shields. In latter, high temperature experiments, bubbled zirconia was added between the outmost radiation shield and the steel shell. A dense alumina tube surrounds the specimens, positioning them and electrically insulating them from the grounded shields and shell. Molybdenum sight tubes penetrate the alumina tube and radiation shields so that sight holes drilled radially into the specimen are visible at the sight ports.

Heater Design

The heaters for this apparatus were largely a matter of evolution. The first family of heaters consisted of molybdenum wire wound on high purity beryllia tubing. Such a helix is then inserted into a beryllia thermocouple protection tube of 3/4" outside diameter and 9" length as indicated in the sketch of Figure 1. These could be fabricated to yield a good radial heat flow pattern and were useful to specimen hot face temperatures of about 2000°C. A temperature limitation of molybdenum on beryllia was found in the 2100 to 2200°C range. Two similar heaters wound with tungsten wire on beryllia yielded similar results. A typical power input at maximum temperature was 125 volts at 20 amps.

The second generation of heaters were of the graphite helix type. A graphite tube 14" long, 3/4" O.D. with a 3/16" wall was machined to form a high resistance helix in a 9" center portion as shown in Figure 2. Water cooled nickel terminals at each end fed power typically at 10 volts and 250 amps to achieve

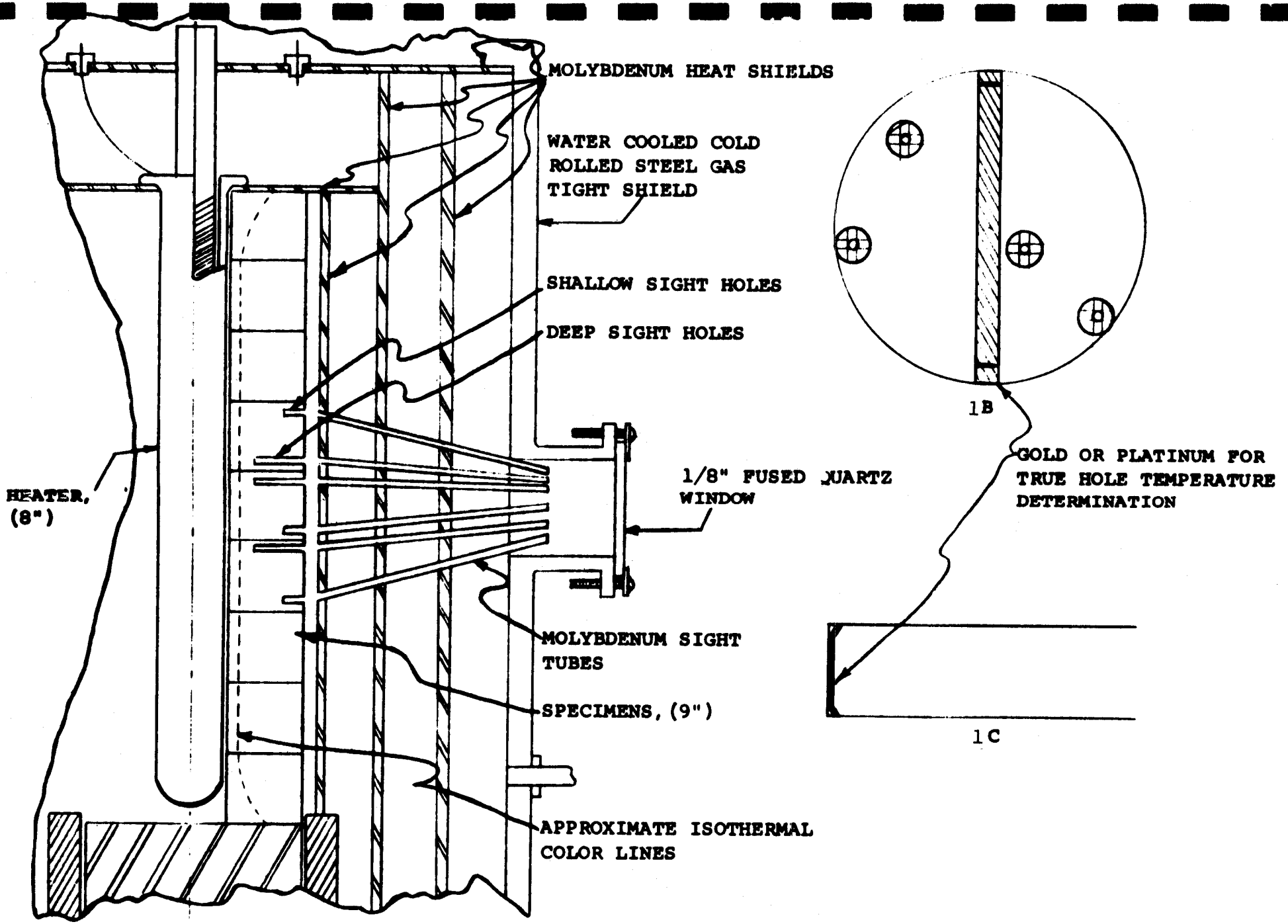

FIGURE 1 Schematic of Sight Hole Geometry

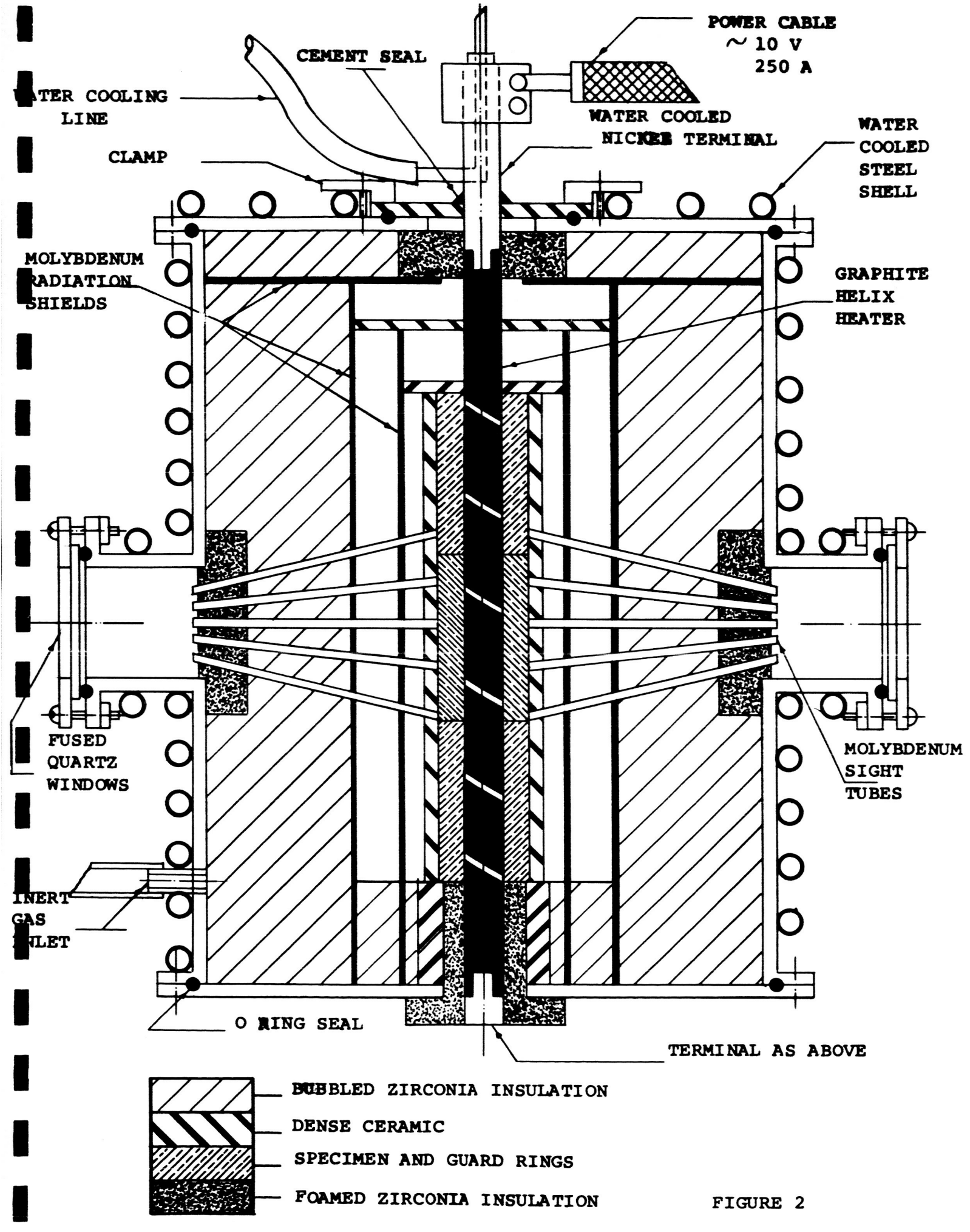
POWER CABLE
~ 10 V
250 A
CEMENT SEAL
WATER COOLING LINE
WATER COOLED NICKEL TERMINAL
CLAMP
WATER COOLED STEEL SHELL
MOLYBDENUM RADIATION SHIELDS
GRAPHITE HELIX HEATER
FUSED QUARTZ WINDOWS
MOLYBDENUM SIGHT TUBES
INERT GAS INLET
O RING SEAL
TERMINAL AS ABOVE
BUBBLED ZIRCONIA INSULATION
DENSE CERAMIC
SPECIMEN AND GUARD RINGS
FOAMED ZIRCONIA INSULATION

FIGURE 2

specimen hot face temperatures at 2300°C. Terminal connections and specimen changing was extremely complex with this geometry. Excellent radial heat flow patterns were achieved, however, as measure optically and visible in the isothermal color lines left in the specimens after measurement.

The heater presently employed is of the graphite hairpin type as shown in Figure 3. This design has the following advantages:

1. Both terminals protrude from the top of the apparatus so that the terminal atmosphere seals need not be distrubed when the specimens are changed from the bottom. The step-wise changes in diameter of the graphite between the hot zone and the terminals serve as thermal radiation shields as well as decreasing electrical resistance in this area, both tending to reduce heat lossed towards the top of the apparatus.

2. Heat losses from the bottom are diminished by elimination of the graphite and metal terminals.

3. The simplicity of the bottom now allows incorporation of thermocouple wells as pictured on one side of Figure 3. In practice sight holes are 180° apart with two sets of thermocouple wells each about 90° from the sight hole.

4. The threaded terminal design eliminates the termal expansion mis-match problems encountered in the graphite helix terminal arrangement.

The high heater currents are transmitted from the brass terminals to the graphite through flat nickel washers butted between the threaded terminal ends and tapped holes in the graphite heater. A dense beryllia plate containing two snug holes for the brass terminal is sealed by a silicone rubber O-ring set into the water cooled steel top plate. Similarly, silicone rubber O-rings are used around the water cooled terminals and clamped against the beryllia plate.

EXPERIMENTAL PROCEDURE

Operation of the test cell is briefly as follows:

1. Sight and thermocouple wells are located and machined into the specimen stack of 9" total height.

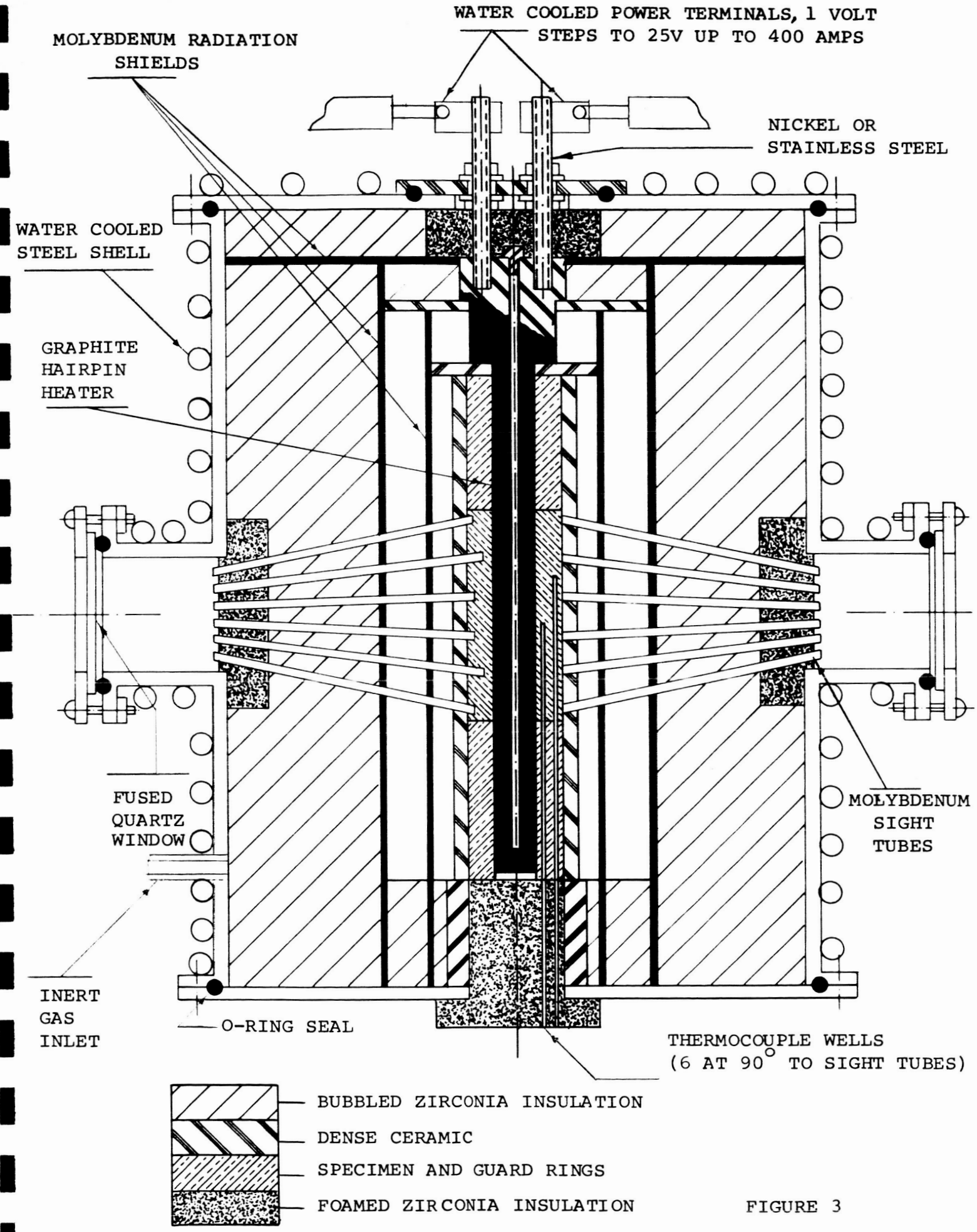
WATER COOLED POWER TERMINALS, 1 VOLT STEPS TO 25V UP TO 400 AMPS
MOLYBDENUM RADIATION SHIELDS
NICKEL OR STAINLESS STEEL
WATER COOLED STEEL SHELL
GRAPHITE HAIRPIN HEATER
FUSED QUARTZ WINDOW
MOLYBDENUM SIGHT TUBES
INERT GAS INLET
O-RING SEAL
THERMOCOUPLE WELLS (6 AT 90° TO SIGHT TUBES)
BUBBLED ZIRCONIA INSULATION
DENSE CERAMIC
SPECIMEN AND GUARD RINGS
FOAMED ZIRCONIA INSULATION

FIGURE 3

2. The specimen are set on the zirconia pedestal and raised into place. A sight hole locating fixture assures alignment vertically and rotationally. A keyed locking device is provided.

3. A vacuum bell is attached at the bottom and the chamber evacuated, or inert gases are introduced below the sight ports. Argon, helium, hydrogen, and dissociated ammonia have been employed.

4. Power is applied in one volt increments periodically to the graphite heaters. Hot face temperatures of 2300°C may be reached in several hours but usually more slowly (8 to 30 hours) to prevent thermal shock damage to the specimens.

5. The apparatus is allowed to come to thermal equilibrium before any measurements are taken. Steady state conditions are assumed when a shallow hole temperature (furthest from the heater) records a straight-line ($\pm$ 5°C) for a 15 minute time interval.

6. At equilibrium, measurements are made of the power input (volts and amperes) and the temperature of the heater and at least two accurately known radial locations within the specimen.

Temperature Measurement

Temperature measurements have been made by several methods:

1. Calibrated optical pyrometer

2. An infra-red radiation pyrometer

3. Tungsten-rhenium thermocouples

The optical and radiation measurements are made in sight holes drilled radially from the outside surface of the specimen to accurately known distances from the hot face. Twelve points are normally measured at each steady state condition, at least 4 at each of two known depths, half at each window. Usually one or more sight holes are drilled through to determine heater temperature. These sight holes are spread over the 3" central section of the 9" high specimen. Normally only small random temperature differences are noted between holes of identical depths. Calibration was accomplished by placing small strips of pure gold and subsequently pure platinum on the isotherms at the flat bottom of the sight holes

and observing the ceramic temperature when the metal melted. Positioning of these strips and the relative spot size of the infra-red pyrometer is indicated in the inserts of Figure 1. Spectral normal emittance as measured with the infra-red radiation pyrometer was found to approach unity in the higher temperature regions for sight holes in high purity but calcia stabilized zirconium dioxide, the ceramic primarily investigated. This would be expected in a sight hole of high depth to width ratio and is also in good agreement with the data on bulk ZrO_2(1)*.

The infra-red radiation pyrometer has been found to be ineffective on current porous ceramic specimens. This instrument has an extremely small area of focus, of the same magnitude or smaller than the diameter of some pores in ceramic foams. Measurements were found to vary greatly depending on if the focus was deep within a pore barely opened when machining the sight hole or truly on the plane (isotherm) as intended. The spread of data is smaller from the "hot wire" optical pyrometer for it is easier to visually average the color at the bottom of a sight hole. The infra-red unit is also far more sensitive to window reflections and angle of incidence to the surface to be measured.

The required number of measurements (up to 12 with optimum alignment) each in duplicate may also be made more quickly with the optical pyrometer then with infra-red unit and yield sufficiently good data for the current program. This compromise allows about four steady state measurements per day or up to two 6 to 8 point determinations in a five day week.

Calculations

Thermal conductivity is calculated from the observed measurements from the equation:

$$K = \frac{q \ln \frac{r_1}{r_2}}{2\pi l \Delta T} \qquad (1)$$

q = rate of heat flow in watts

l = length of sample through which q is flowing radially (cm)

r_1 and r_2 = the radii of any two different sight holes (any units)

ΔT = the measured temperature difference between the bottoms of holes r_1 and r_2 (C^o).

*References appear under the heading REFERENCES

The following assumptions are made:

1. Steady state conditions are achieved

2. Longitudinal heat flow and end effects are negligible

3. Circular isotherms are established throughout the specimen length.

Steady state attainment has already been mentioned. Heat losses from the specimen ends are real, therefore, some longitudinal heat flow does exist. This is not true for the central 3" of the specimen, optical measurements and isothermal color lines after measurement confirm that radial heat flow is established over more than 6" of the specimen length. The insulating qualities of the specimen ends, which may be thought of as guard rings, coupled with excellent thermal insulation above and below the specimen tend to keep such losses low. Calculation for a one centimeter segment of a nine inch sample results in dividing the measured "q" by 23, reducing somewhat the magnitude of the error. Since this error is a constant and cancels in comparing two materials this method is sufficient for the present application. Similarly voltmeter and ammeter errors (± 2%) are constant and cancel in comparative data. Measurement errors (r_1 and r_2 ± 2%) and temperature measurement errors (± 3%) are the major causes for the observed spread in the data (about ± 6%).

RESULTS

Figure 4 is a plot of thermal conductivity versus temperature for several samples measured with the apparatus as described. Data points are shown, for example, for several runs on one set of NBC dense zirconia specimens, runs 4 - 6 using a molybdenum wire wound heater and run 17 using a graphite helix heater. Acceptable reproducibility may be noted, even with this major change in heater design, power supply and power input metering. A curve calculated from SRI data reported by Pears (1)* at last years conference is included for comparison as shown by the open circles and dotted line.

Conductivity curves are shown for two types of zirconia foams. Foam Zr6 was a low density impure material (8600 ppm) of low initial conductivity which tended to densify above 1600°C and

*References appear under the heading REFERENCES

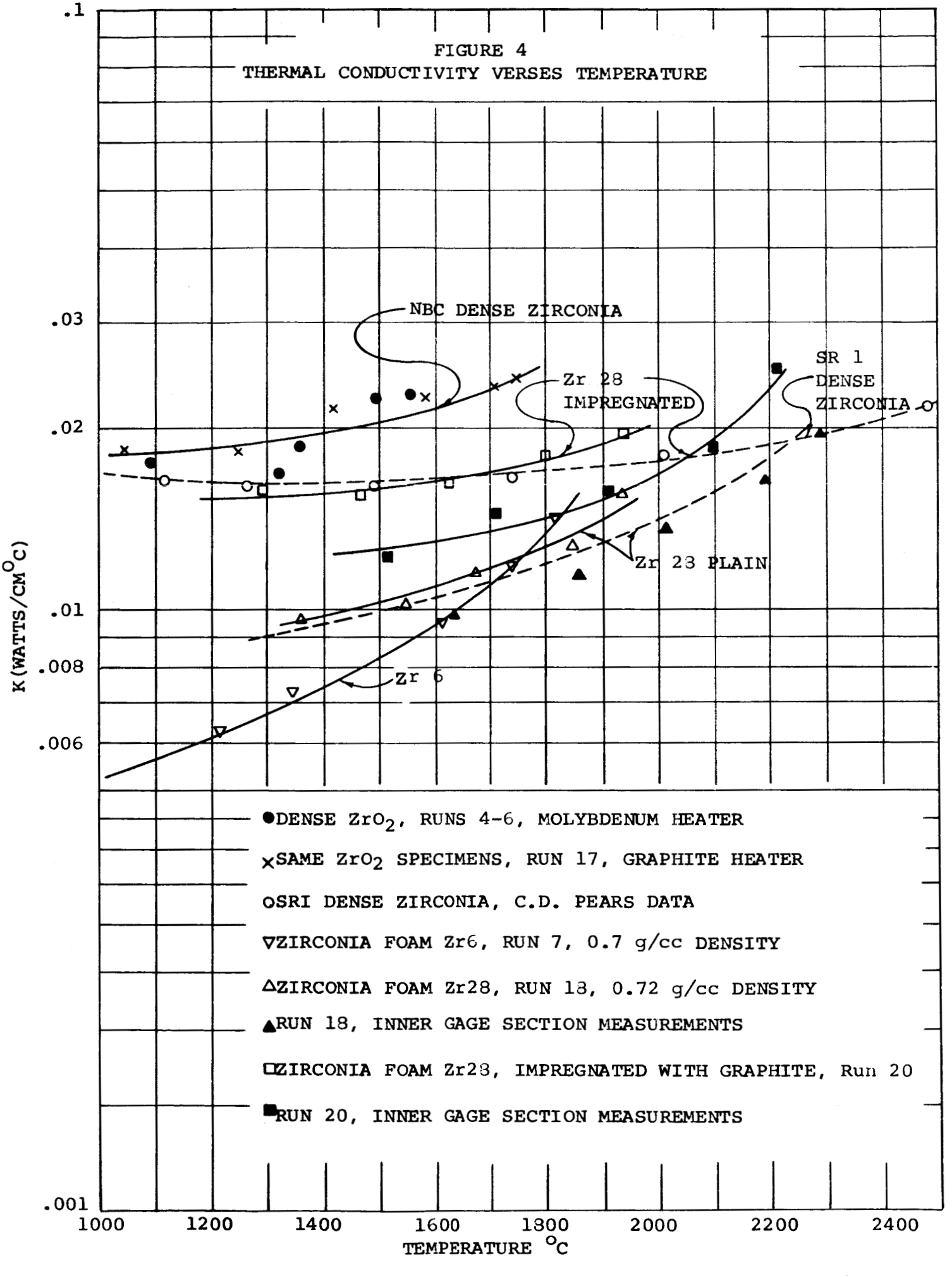
FIGURE 4
THERMAL CONDUCTIVITY VERSES TEMPERATURE
.1
.03
.02
.01
.008
.006
.001
K (WATTS/CM °C)
1000
1200
1400
1600
1800
2000
2200
2400
TEMPERATURE °C
NBC DENSE ZIRCONIA
Zr 28 IMPREGNATED
SR 1 DENSE ZIRCONIA
Zr 23 PLAIN
Zr 6
●DENSE ZrO2, RUNS 4-6, MOLYBDENUM HEATER
×SAME ZrO2 SPECIMENS, RUN 17, GRAPHITE HEATER
○SRI DENSE ZIRCONIA, C.D. PEARS DATA
▽ZIRCONIA FOAM Zr6, RUN 7, 0.7 g/cc DENSITY
△ZIRCONIA FOAM Zr28, RUN 18, 0.72 g/cc DENSITY
▲RUN 18, INNER GAGE SECTION MEASUREMENTS
□ZIRCONIA FOAM Zr28, IMPREGNATED WITH GRAPHITE, Run 20
■RUN 20, INNER GAGE SECTION MEASUREMENTS

degrade above 1800°C. Foam Zr28 of 700 ppm impurity level at a similar density has a slightly higher conductivity initially, but does not degrade significantly even at 2300°C, thereby crossing the curve of Zr6. Open triangles are data points calculated from a gage section between 0.125 and 0.500" from the hot face. Solid triangles are calculated from the .125" section adjacent to the heater and consistantly yield about 10% lower values. This suggests the measured heater temperature is not the same as the specimen hot face temperature but is somewhat lower.

An identical stack of Zr28 specimens was vacuum impregnated with colloidal graphite; dried and measured as indicated by the squares in Figure 4. Conductivity is increased as would be expected, however, the argon purge technique used in this run 20 allowed entrappment of air within the foam and therefore oxidation of the graphite, especially in the inner gage sections. The wide spread between solid and open squares and the sharp upturn to radiation conduction near the heater was readily understandable when the specimens were examined after the run. A re-evaluation by evacuating the chamber and backfilling with argon or helium, if necessary, is in progress.

FUTURE WORK

Measurements to date have indicated the feasibility of the apparatus and its ability to yield data sufficient for the current requirements. Evaluation of many types of ceramic foams are planned. Samples are being prepared with a variety of potential thermal radiation barrier phase incorporated within the pores. Tungsten flake, tungsten coated hollow zirconia spheres and solid particles, molybdenum deposites and continuous, discontinuous and gasous phases of carbons and hydrocarbons are being introduced into ceramic foams and their effect on high temperature conductivity measured. The graphite hairpin design is being found useful to about 2400°C, in the argon atmosphere, above this conduction through ionized argon within the heater slot causes high local temperature (above the melting point of zirconia, 2700°C). If further temperature increases are desired, a variation of the helix design will be necessary.

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REFERENCES

(1) Pears, C. D., "Some 'Standard' Specimens for High Temperature Thermal Conductivity Apparatuses", THE SECOND CONFERENCE ON THERMAL CONDUCTIVITY, Held at Division of Applied Physics N.R.C., Ottawa, October 10 - 12, 1962, pg. 342.

Appendix II Sample Calculation

Thermal conductivity is calculated as follows:

$$K = \frac{q \ln \frac{r_1}{r_2}}{2\pi L \Delta T}$$

typical measurements are:

r_1 radius of deep hole 1.270 cm

r_2 radius of shallow hole 2.222 cm

L total specimen length 22.85 cm

q power input, 10.0 volts
258 amps
q = 2580 watts

ΔT temperature difference

Tr_1 1745°C

Tr_2 1375°C
$\Delta T = 470C^{\circ}$

$$K = \frac{2580\ (.5596)}{2(3.1416)22.85(470)} = .0213 \text{ watts/cm}^{\circ}\text{C}$$

$$.0213\ (\text{W/cm}^{\circ}\text{C}) \times 693.4 \frac{\text{BTU/ft}^2\text{/hr/in/}^{\circ}\text{F}}{\text{W/cm}^{\circ}\text{C}} =$$

$K = 14.75\ \text{BTU/ft}^2\text{/hr/in/}^{\circ}\text{F}$